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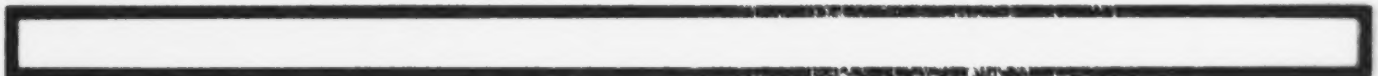
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Bioassay Sampling System (MIBAS) for
At-Sea Incineration Testing

Battelle Columbus Labs., OH

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THE DEVELOPMENT OF THE MARINE INCINERATION BIOASSAY
SAMPLING SYSTEM (MIBAS) FOR AT-SEA INCINERATION TESTING

by

William H. Piispanen
Battelle Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

Merrill D. Jackson
Air and Energy Engineering Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

and

David P. Redford
Office of Marine and Estuarine Protection
Office of Water
U.S. Environmental Protection Agency
Washington, DC 20460

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16. ABSTRACT The paper discusses the development of the Marine Incineration Bioassay Sampling System (MIBAS) for at-sea incineration testing, as part of EPA's overall evaluation of the potential benefits and risks associated with the incineration of hazardous wastes at sea. The related strategy focuses on the acquisition of scientific information and on the development of new techniques designed to expand the knowledge of: 1) the chemical nature of incinerator emissions; 2) the behavior and fate of incinerator emission plumes; 3) the possible extent of exposure of marine organisms to these emissions; and 4) the possible environmental consequences of such an exposure. An integral part of this strategy is the formation of a firm scientific basis for the assessment of environmental risk through the development of a rational, scientifically defensible methodology for this assessment. The program includes three major study areas: methods development, at-sea research burns, and long-term risk assessment research. To date, research has been in the first study area and has included: development of an emissions sampling technique for toxicity tests, development of toxicity tests, land-based incinerator tests, and determining appropriate sampling procedures for chemical characterization.			
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1.0 INTRODUCTION

As part of the Environmental Protection Agency's (EPA) overall strategy developed to evaluate both the potential benefits and risks associated with the incineration of hazardous wastes at sea, an overall environmental research strategy has been formulated (U.S. EPA, 1985). This strategy focuses on the acquisition of scientific information and on the development of new techniques designed to expand our knowledge of: 1) the chemical nature of incinerator emissions; 2) the behavior and fate of incinerator emission plumes; 3) the possible extent of exposure of marine organisms to these emissions; and 4) the possible environmental consequences of such an exposure. An integral part of this strategy is the formation of a firm scientific basis for the assessment of environmental risk through the development of a rational, scientifically defensible methodology.

The program actually includes three major study areas: 1) Methods Development, 2) At-Sea Research Burns, and 3) Long Term Risk Assessment Research. To date, research has been in Study Area 1 and has included:

- Development of an emissions sampling technique for toxicity tests
- Development of appropriate toxicity tests
- Land based incinerator testing
- Determining appropriate sampling procedures for chemical characterization

This paper will discuss the developments in this project to date.

2.0 DEVELOPMENT OF A SAMPLING TECHNIQUE OF AT-SEA INCINERATION EMISSIONS SAMPLING FOR TOXICITY TESTING

The development of a system for toxicity testing involved the refinement of existing methods and the development of new techniques geared to the quantitative sampling of actual emissions from high-temperature incinerator stacks. The collected sample is diluted with seawater

to reach the maximum realistic concentration expected if the gaseous plume from an incinerator ship were to impinge on the sea surface. The resultant diluted sample is adjusted so that, when introduced to marine bioassays, only the effects of toxic products of combustion are assessed. These samples are then tested by an array of validated, relevant marine bioassays.

Since the purpose of the sampling system is to provide samples for aquatic toxicity tests, the system has to produce samples which simulate ocean water exposed to incinerator emissions. Consequently, the sampling system was designed to draw emission gases from an incinerator flue and mix these gases with seawater to trap sample constituents. Since this sampling process will collect hydrochloric acid (HCl) and water vapor, the system also has to accommodate the extra volume of water and acid which will be collected. Additional considerations in the design of the emissions sampling system included ease of transportation, availability of materials, completeness of collection, corrosion protection, ruggedness, and the following emission gas and seawater mix volumes specified by EPA:

- Emission from three incinerators:
 $66,000 \text{ m}^3/\text{hr} \times 3 = 198,000 \text{ m}^3/\text{hr}$
- Volume of seawater potentially exposed under plume:
 $5,556 \text{ m/hr} \times 1,200 \text{ m} \times 0.01 \text{ m} = 66,672 \text{ m}^3/\text{hr}$
 (speed of ship) x (plume width) x (mixing depth)
- Resulting gas dilution: approximately 0.03 m^3 gas/10% seawater.

Then, using a dilution safety factor of x10 and a sampling collection efficiency of 50 percent (x2 factor), the sample size was estimated as $0.6 \text{ m}^3/10\%$ seawater. For a 3 hour sample at $4 \text{ m}^3/\text{hr}$, the resulting concentration would require dilution of the 10% of seawater by 20 to achieve 0.6 m^3 of emission, or a total of 200% of seawater to be used for toxicity testing per sample.

3.0 DEVELOPMENT OF SAMPLING SYSTEM

The sampling system chosen for this program was based on the EPA Source Assessment Sampling System (SASS) impinger train modified for direct seawater impingement and condensation. Since this system is a modification of an existing system, ruggedness, corrosion protection, availability of materials, and ease of transportation have already been demonstrated. The train, however, did require testing for completeness of collection in a seawater matrix. The modified system, was renamed the Marine Incineration Bioassay Sampling (MIBAS) system, and five prototype sampling systems were developed at Battelle.

The MIBAS design uses three impingement stages to maximize exposure of the gaseous emission sample to the collecting liquid, seawater. The basic design, shown in Figure 1, incorporates a heated, flexible Teflon® line and cooling coil condenser between the stack probe and impinger stages to condition the gas stream. The cooled gas (<20°C) enters the first impinger stage, a tube with four openings of approximately 0.4-cm diameter. These large openings allow direct impingement of gas and particulate matter. The second impinger is an open tube. Any particulate material should be trapped in the first two impingers. The third impinger uses a coarse frit on the impinger tube to improve gas/liquid contact.

The three impingers each have a total liquid capacity of 2.5 liters, and each initially contains 500 ml of filtered seawater. The MIBAS bioassay sample includes the liquid in these three impingement stages plus any particulate and moisture collected from the flue gas sampled. The train is rinsed with filtered seawater and added to the sample. Rinsings include the probe, flexible Teflon line, condenser coil, and three impinger chambers.

Immediately following the three impingers is a high capacity XAD-2 resin cartridge (120 g resin) to collect organic analytes passing through the impingers. In the development studies with the MIBAS train, the sample was collected on resin to show any breakthrough from the impingers. A solvent rinse (methylene chloride) of the total train was used to measure any organic species adhering to the glassware, which could not be rinsed free using seawater.

A fourth impinger containing 0.5 M KOH and bromocresol purple indicator was used to show HCl breakthrough which could potentially damage the pumping system.

The MIBAS system operates at a nominal velocity of 0.056 m³/min. (2 cfm) which samples approximately 10 m³ of flue gas during a 3-hr experiment. At gas-phase moisture levels expected in marine incineration discharges, this corresponds to approximately 0.75 - 1 liter of condensed moisture in the train. The total liquid catch, including rinses, is approximately 3 liters.

In the combustion system tests, a dual-chamber probe that employs both water- and air-cooled jacketing is needed to dissipate the high thermal energy found when sampling this source. Probe temperatures as high as 1200°C are often encountered. The external water jacket is used to dissipate the thermal energy, and internal air cooling is used to control the probe temperature within reasonable limits. The probe is approximately 6.4m (21 feet) long and is glass lined. Three of these probes have been assembled at Battelle.

4.0 LABORATORY TESTING OF THE MIBAS SYSTEM

The following section describes the tests performed and the two combustion systems used to demonstrate the performance of the MIBAS train. The initial development experiments were performed with a synthetic flue gas generated by heating clean laboratory air to 248°C (500°F) using a muffle furnace and adding principal fixed gases, including HCl, at levels found in previous at-sea incineration tests. The second combustion system used was an actual pilot plant combustion system fired with No. 2 fuel oil, the incineration support fuel used on the ocean-going incineration vessels. This small scale research incinerator is capable of up to 5.3×10^8 J/hr (0.5×10^6 Btu/hr) heat input to the furnace.

During both development tests, a gas-phase spiking system developed by Battelle for the U.S. Environmental Protection Agency (Cooke et al., 1984) was used to inject known quantities of selected Principal Organic Hazardous Constituents (POHCs) continuously into the flue gas stream. Thus, known concentrations of POHC (e.g., dioxin

and PCB) in flue gas were available for testing. Table 1 lists analytes used as POHC simulants.

The POHC flow rate was maintained at about 16.5 cc per hr during a 3-hr run. Addition of HCl was maintained at 3 percent Volume/Volume ratio. The CO₂ level in the exit gases was checked periodically using a nondispersive infrared analyzer. The CO₂ level remained stable at about 12 percent during a run. Water vapor was added to maintain about 10 percent H₂O in the gas stream. This water vapor rate corresponds to approximately 275 cc H₂O per hour.

Five tests were planned to demonstrate the performance of the MIBAS train under simulated conditions. Recovery efficiencies for the target compounds from the continuous extraction of seawater ranged from 73 percent for 1234-TCDD to 98 percent for 1245-TCB. The recovery of target analytes from XAD-2 ranged from 90 percent for 1234-TCDD to 97 percent for 1245-TCB. The recoveries of target compounds from both techniques were considered acceptable.

Additional tests with the Battelle Multifuel Furnace (MFF) were carried out to develop collection and handling protocols along with a bioassay system shakedown study. The Battelle MFF is 9.5 cm (24 in.) in diameter and 24 cm (60 in.) long, refractory-lined, and water-cooled. The burner has movable vanes so combustion-air swirl can be continuously varied while operating from no swirl to high swirl. An air preheater is available to heat combustion air to 260°C(500°F). Immediately downstream of the combustion zone, air-cooled tubes simulate the superheater or reheater sections of a boiler. Typically, the tubes are operated at temperatures of 600-480°C (1,100-900°F). Sampling ports for both gaseous and particulate emissions are provided in an air-cooled duct following the tubes.

In the second study, the combustor was fired with No. 2 distillate fuel oil at 6.3 to 7.9×10^8 J/hr (600,000 to 750,000 Btu/hr). The combustor is designed to give a residence time of about 1.0 sec in the main section.

The tests conducted during the shakedown study with the MFF were a follow-up to tests conducted with the synthetic fuel gas mixture discussed earlier, except that a number of different procedures were employed: 1) two MIBAS trains were run simultaneously with the

MFF; 2) the hot flue gas entering the trains was drawn from the MFF; 3) the flue gases were withdrawn from the furnace using quartz-lined probes cooled with water and air; 4) exposed samples were used directly for the toxicity tests (no POHC spiking was performed); and 5) each set of two MIBAS trains was run with and without HCl addition. All tests were recovered for bioassay testing and methods development.

5.0 BIOASSAY STUDIES

The experimental design of the shakedown studies included two control and two experimental treatments. The control treatments consisted of natural seawater (Narragansett Bay seawater) and concentrated brine (128 ‰) that was diluted to 30 ‰ with deionized water. This latter solution was termed "reconstituted brine." The two experimental treatments consisted of reconstituted brine to which was added the fuel oil gaseous emissions and the fuel oil emissions spiked with HCl, using the MIBAS system, for purposes of simulating the pH of a highly chlorinated hazardous waste burn. Emissions were collected daily, adjusted for water quality, and diluted with seawater to a maximum concentration of 2 percent of the original unadjusted MIBAS sample. Five biological tests were conducted for the shakedown testing: the sea-urchin fertilization test which was employed as a sensitive short-term (approximately 4 hr) screening test; and short-term chronic tests (2 to 7 days) on a fish (Menidia beryllina), a crustacean (Mysidopsis bahia), an alga (Champia parvula), and a worm (Dinophilus gyrociliatus). All chronic tests were conducted as static renewal tests and were monitored daily for salinity, temperature, and dissolved oxygen. All bioassay studies performed during the shakedown studies were conducted in EPA's mobile bioassay laboratory.

6.0 LAND-BASED INCINERATOR TESTING

As a final shakedown of the MIBAS system, a land-based field trial was conducted at the EPA Combustion Research Facility (CRF) in Jefferson, Arkansas. The CRF includes two small incinerators and

ancillary emissions control systems. For the MIBAS tests, a liquid injection incinerator firing at approximately 3.2×10^9 J/hr (3×10^6 Btu/hr) was used. A blend of an Arochlor transformer oil and standard diesel fuel was used as the liquid fuel. An additional propane-fired burner was used to maintain high combustion temperatures. The combustor is refractory lined and is capable of firing approximately 45.4 kg/hr (100 lb/hr) of liquid fuel.

Seven consecutive tests were made between March 5 and 11, 1986. All seven tests successfully demonstrated the feasibility of the field operability of the MIBAS sampling system and the Mobile Bioassay Facility. As a result of these tests, Standard Operating Procedures (SOPs) are being revised to correct any observed problems. A full scale at-sea test series is planned.

7.0 REFERENCES

Cooke, M., DeRoos, F., and Rising, B. 1984. Hot Flue Gas Spiking and Recovery Study for Tetrachlorodibenzodioxins (TCDD) Using Modified Method 5 and SASS Sampling with a Simulated Incinerator. Report EPA-600/2-84-159(NTIS PB 85 115145).

U.S. Environmental Protection Agency, 1985. Incineration-At-Sea Research Strategy. Office of Water. Washington, DC.

TABLE 1. ANALYTES USED IN THE MIBAS DEVELOPMENT TESTS

Chemical Name	Abbreviation Used
1,2,3-Trichlorobenzene	123-TCB
1,2,4,5-Tetrachlorobenzene	1245-TCB
4-Monochlorobiphenyl	4-MCB
Pyrene	PYR
3,3',4,4'-Tetrachlorobiphenyl	33'44'-TCB
Pentachlorophenol	PCP
Chrysene	CHR
Benzo[<i>k</i>]fluoranthene	BkF
Benzo[<i>a</i>]pyrene	BaP
2,2',3,3',5,5',6,6'-Octachlorobiphenyl	OCB
1,2,3,4-Tetrachlorodibenzo-p-dioxin	1234-TCDD
Decachlorobiphenyl	DCB

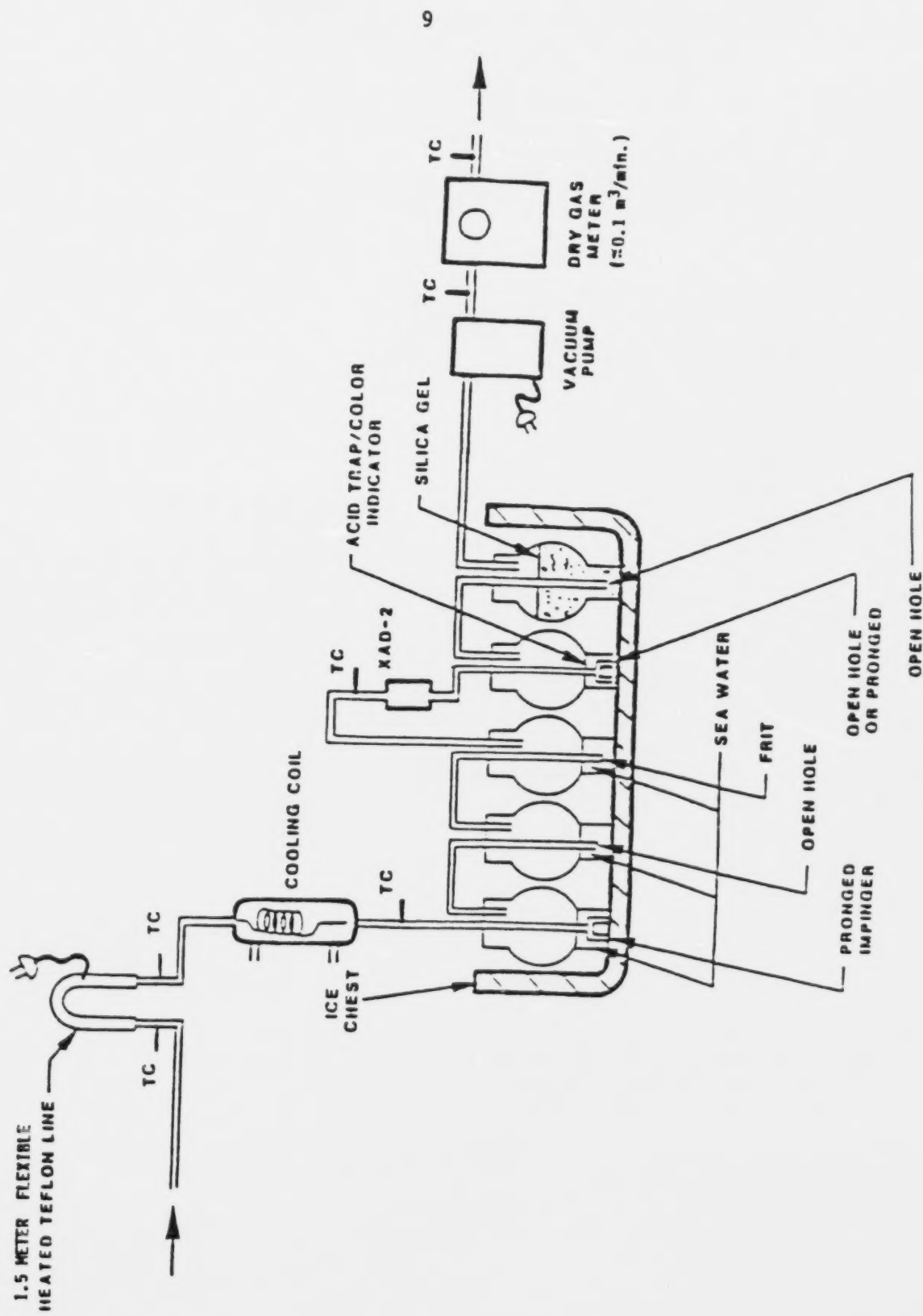


FIGURE 1. MTBAS TRAIN

TABLE 2. LIST OF FUEL OIL COMBUSTION EMISSION SAMPLES
(MIBAS) GENERATED DURING THE PERIOD FROM
JUNE 19-26, 1985 AT THE BATTELLE COLUMBUS
LABORATORIES

Date	Sample Designation
6-19-85	MIBAS-0-No HCl
6-20-85	MIBAS-1-No HCl MIBAS-2-HCl
6-21-85	MIBAS-3-No HCl MIBAS-4-HCl
6-22-85	MIBAS-5-No HCl MIBAS-6-HCl
6-23-85	MIBAS-7-No HCl MIBAS-8-HCl
6-24-85	MIBAS-9-No HCl MIBAS-10-HCl
6-25-85	MIBAS-11-No HCl MIBAS-12-Blank MIBAS-13-HCl
6-26-85	MIBAS-14-No HCl MIBAS-15-Blank MIBAS-16-HCl